

Sodium *p*-nitrophenolate tetrahydrateS. Brahadeeswaran,<sup>a†</sup> H. L. Bhat,<sup>a</sup> J. N. Sherwood<sup>b</sup> and R. M. Vrcelj<sup>c\*</sup><sup>a</sup>Department of Physics, Indian Institute of Science, Bangalore 560 012, India, <sup>b</sup>Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, and <sup>c</sup>Combinatorial Centre of Excellence, Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England

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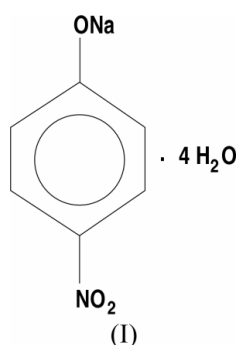
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## Key indicators

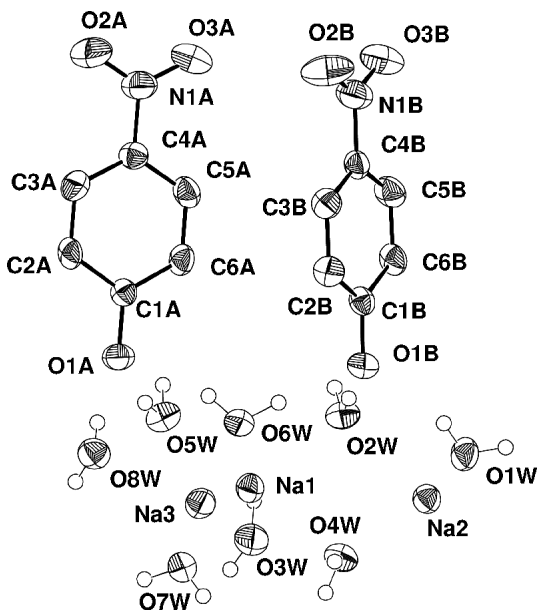
Single-crystal X-ray study  
*T* = 123 K  
Mean  $\sigma(C-C)$  = 0.003 Å  
*R* factor = 0.041  
*wR* factor = 0.101  
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The structure of sodium *p*-nitrophenolate tetrahydrate, Na<sup>+</sup>·C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub><sup>-</sup>·4H<sub>2</sub>O, is presented. The nature of the hydrogen and coordination bonds in this structure is discussed and compared with that of sodium *p*-nitrophenolate dihydrate.Received 12 April 2002  
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## Comment

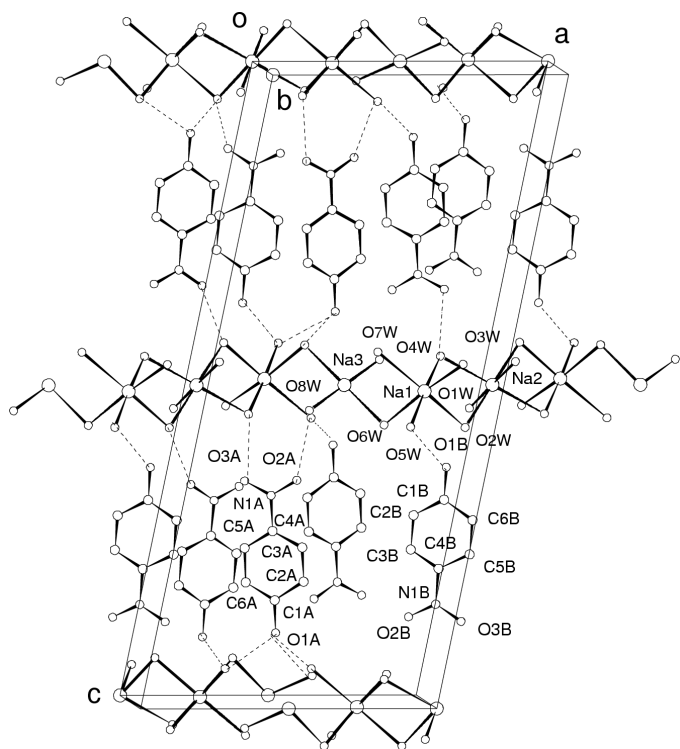
The influence of solvents on crystallization in the formation of new structures of organic compounds is well known and this effect can pose serious problems when crystallizing materials for non-linear optical (NLO) applications. Minemoto *et al.* (1994) have reported problems associated with the selection of solvents for growing crystals of sodium *p*-nitrophenolate dihydrate (NPNa·2H<sub>2</sub>O), a recent NLO material. This orthorhombic dihydrate system (Minemoto *et al.*, 1992) was formed when crystallized from methanol solution, whereas the water solvent gave transparent crystals in solution, but these lost their transparency on exposure to air. We have carried out further investigations on the growth of NPNa with water as solvent. During the course of this study, we found two types of crystals, *viz.* monoclinic tetrahydrate and monoclinic monohydrate, which are easily distinguishable by their colour, the former being yellow and the latter being red-brown. Some mention of the tetrahydrate form has already been made in a previous report (Brahadeeswaran *et al.*, 1998). The present study reports the structure of this tetrahydrate form, (I), in more detail.



In the tetrahydrate form, we have observed extensive hydrogen bonding. Both O1A and O1B of the nitrophenoxy ions in the asymmetric unit shown in Fig. 1 are hydrogen bonded to four O atoms of the solvate water molecules. The O atoms of the NO<sub>2</sub> group also form hydrogen bonds with water molecules (Table 1). The availability of relatively more water molecules, as well as Na<sup>+</sup> ions in special positions in this form (see Fig. 2), alters the hydrogen-bonding patterns, compared to the well studied dihydrate form, in which the water molecule is hydrogen bonded only to atom O1 of the nitro-



**Figure 1**  
The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids. [Please provide revised figure with labels shifted off the ellipsoids.]



**Figure 2**  
Packing diagram of the crystal structure of the title compound.

phenolate (Minemoto *et al.*, 1992). While the Na atom in the tetrahydrate structure forms regular coordination bonds with six neighbouring OW atoms, resulting in octahedral stacking along the crystallographic *a* axis, the Na<sup>+</sup> cation in the dihy-

drate form interacts only with atom O2 of the NO<sub>2</sub> group and atoms O3 and OW.

## Experimental

The title compound was synthesized from equimolar solutions of *p*-nitrophenolate and sodium hydroxide in water. Single crystals of the tetrahydrate form were grown from aqueous solution by solvent evaporation at 300 K. These crystals were found to nucleate and grow to suitable size for examination after 1 d of solution preparation.

### Crystal data

Na<sup>+</sup>·C<sub>6</sub>H<sub>4</sub>NO<sub>3</sub><sup>-</sup>·4H<sub>2</sub>O  
*M<sub>r</sub>* = 233.16  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 11.844 (2) Å  
*b* = 6.8736 (12) Å  
*c* = 25.939 (6) Å  
 $\beta$  = 101.038 (17)°  
*V* = 2072.6 (7) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.49 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.44 Mg m<sup>-3</sup>

*D<sub>m</sub>* measured by flotation in CHBr<sub>3</sub>/  
 C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>  
 Mo *K*α radiation  
 Cell parameters from 25  
 reflections  
 $\theta$  = 12.0–15.1°  
 $\mu$  = 0.17 mm<sup>-1</sup>  
*T* = 123 (2) K  
 Block, yellow  
 0.3 × 0.2 × 0.2 mm

### Data collection

Rigaku AFC-7S four-circle  
 diffractometer  
 $\omega$  scans  
 5184 measured reflections  
 4641 independent reflections  
 4267 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.016

$\theta_{\max}$  = 27.5°  
*h* = 0 → 15  
*k* = 0 → 8  
*l* = -33 → 31  
 3 standard reflections  
 every 150 reflections  
 intensity decay: 4.0%

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR* (*F*<sup>2</sup>) = 0.101  
*S* = 1.12  
 4641 reflections  
 370 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 2.0621P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

**Table 1**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3W—H9...O1A <sup>i</sup>	0.84 (3)	2.00 (3)	2.828 (2)	166 (3)
O3W—H10...O1B <sup>i</sup>	0.85 (3)	1.93 (3)	2.765 (2)	168 (2)
O5W—H11...O8W	0.86 (3)	1.92 (3)	2.769 (2)	170 (3)
O5W—H12...O3A <sup>ii</sup>	0.80 (3)	2.12 (3)	2.916 (2)	171 (3)
O7W—H13...O1B <sup>i</sup>	0.82 (3)	1.97 (3)	2.781 (2)	167 (2)
O1W—H14...O6W	0.86 (3)	1.93 (3)	2.763 (2)	164 (2)
O6W—H15...O2B <sup>iii</sup>	0.86 (3)	2.11 (3)	2.924 (2)	158 (3)
O2W—H16...O1A <sup>iii</sup>	0.86 (3)	2.00 (3)	2.857 (2)	176 (3)
O7W—H17...O3B <sup>iv</sup>	0.85 (3)	2.05 (3)	2.891 (2)	170 (2)
O6W—H18...O1W <sup>v</sup>	0.83 (3)	1.96 (3)	2.778 (2)	166 (3)
O1W—H19...O1B <sup>vi</sup>	0.81 (3)	2.01 (3)	2.753 (2)	153 (3)
O2W—H20...O2A <sup>ii</sup>	0.82 (3)	2.10 (3)	2.908 (2)	170 (3)
O8W—H21...O1A	0.79 (3)	2.01 (3)	2.781 (2)	164 (3)
O8W—H22...O4W <sup>vii</sup>	0.81 (3)	1.99 (3)	2.791 (2)	171 (3)
O4W—H23...O1A <sup>i</sup>	0.91 (3)	1.85 (3)	2.744 (2)	171 (2)
O4W—H24...O1B <sup>viii</sup>	0.83 (3)	2.04 (3)	2.856 (2)	168 (3)

Symmetry codes: (i) 1 - *x*, 2 - *y*, - *z*; (ii) 1 - *x*, *y* - ½, ½ - *z*; (iii) *x*, *y* - 1, *z*; (iv) *x* - 1, ½ - *y*, *z* - ½; (v) - *x*, 1 - *y*, - *z*; (vi) *x* - 1, *y*, *z*; (vii) *x*, 1 + *y*, *z*; (viii) 1 - *x*, 1 - *y*, - *z*.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *INSIGHTII* (Biosym Technologies, 1995) and *Xtal\_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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